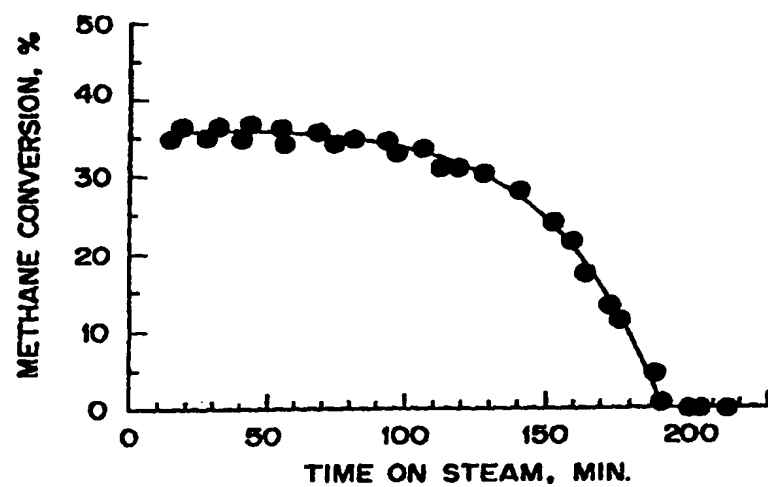


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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01B 3/26, D01F 9/127	A1	(11) International Publication Number: WO 99/43609 (43) International Publication Date: 2 September 1999 (02.09.99)																				
(21) International Application Number: PCT/US99/03572 (22) International Filing Date: 19 February 1999 (19.02.99) (30) Priority Data: 60/075,819 24 February 1998 (24.02.98) US 09/231,861 14 January 1999 (14.01.99) US (71) Applicant: NIAGARA MOHAWK POWER CORPORATION [US/US]; 300 Erie Boulevard West, Syracuse, NY 13202 (US). (72) Inventors: AMIRIDIS, Michael, D.; 2622 Forest Drive, Columbia, SC 29204 (US). BERNALES, Cicero, A.; 5003 Saddlebrook Drive, Fayetteville, NY 13066 (US). (74) Agent: MARJAMA, Owen, D.; Wall Marjama Bilinski & Burr, Suite 400, 101 South Salina Street, Syracuse, NY 13202 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>																				
(54) Title: CARBON FILAMENT PRODUCTION VIA THE DIRECT CRACKING OF HYDROCARBONS																						
 <table border="1"><caption>Data points estimated from the graph</caption><thead><tr><th>Time on Steam (min)</th><th>Methane Conversion (%)</th></tr></thead><tbody><tr><td>0</td><td>35</td></tr><tr><td>25</td><td>35</td></tr><tr><td>50</td><td>36</td></tr><tr><td>75</td><td>35</td></tr><tr><td>100</td><td>34</td></tr><tr><td>125</td><td>32</td></tr><tr><td>150</td><td>25</td></tr><tr><td>175</td><td>10</td></tr><tr><td>200</td><td>2</td></tr></tbody></table>			Time on Steam (min)	Methane Conversion (%)	0	35	25	35	50	36	75	35	100	34	125	32	150	25	175	10	200	2
Time on Steam (min)	Methane Conversion (%)																					
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100	34																					
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150	25																					
175	10																					
200	2																					
(57) Abstract <p>A process for producing carbon filaments or fibers and substantially pure hydrogen by contacting a stream of a hydrocarbon gas with a nickel or nickel-copper containing catalyst at a temperature in the range of about 400 to 900 °C. This results in the conversion of the hydrocarbon gas to carbon and substantially pure hydrogen. The carbon filaments or fibers deposited on the catalyst are a high value material which has separate utility for electrochemical and fuel storage applications, and is recovered for further use.</p>																						

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CARBON FILAMENT PRODUCTION VIA THE DIRECT CRACKING OF HYDROCARBONS

Field of the Invention

This invention relates generally to the production of carbon and hydrogen, and more specifically to carbon filament production by the direct cracking of hydrocarbons such as methane and natural gas.

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Background of the Invention

Significant progress made in fuel cell technologies during the past decade has prompted exploration of replacing traditional central large power plants with so-called distributed power generators, consisting of a hydrogen generator and a
10 membrane fuel cell power plant. This latter technology generates electricity at locations where it is aimed to be used, and therefore, eliminates the loss of electricity during its transmission. In addition, a fuel cell process does not emit any environmental pollutants such as NO_x and SO_x which are combustion by-products. Such a process becomes attractive for the automobile industry as well, since vehicles
15 can be propelled by electricity produced from an on-board fuel cell power plant rather than by an internal combustion engine.

The current proton-exchange membrane (PEM) fuel cells utilize hydrogen as the energy source and require essential elimination (ideally below 20 ppmv) of carbon monoxide from the hydrogen stream to prevent poisoning of the
20 electrocatalyst. Hydrogen is typically produced through steam reforming, partial oxidation or autothermal reforming of natural gas. In all these cases, however, carbon monoxide is a co-product, which has to be converted into carbon dioxide in subsequent steps which adds to the cost of the produced hydrogen.

An alternative route is to directly crack the hydrocarbon fuel into hydrogen
25 and carbon. In this case, the formation of carbon oxides is avoided and the need for downstream reactions such as water-gas shift and selective oxidation for the conversion of carbon monoxide to carbon dioxide is eliminated. Surprisingly, this approach has not been extensively studied. While commercial processes exist that utilize thermal cracking of methane at extremely high temperatures for the

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production of acetylene and carbon black, hydrogen production via the catalytic cracking of methane has been only briefly considered in the past. The carbon black material produced from these existing commercial processes is not filamentous or fibrous in nature. As such, it contains no added value other than the marginal value for typical end-uses or applications of carbon black. The carbon produced in this invention is of high value. In a commercial operation using this invention, the high value carbon produced can be continuously removed using fluid bed or moving bed reactors before regenerating the catalyst bed, if necessary.

In U.S. Patent 3,361,535 high temperature catalytic cracking of methane is taught. The process taught by the 3,361,535 patent, however, results in the production of undesirable carbon monoxide co-product which requires elaborate additional processing for its conversion to carbon dioxide and results in additional cost.

Recently, Muradov *Int. J. Hydrogen Energy* 18,211(1993), studied the use of iron and nickel oxides supported on alumina as catalysts for the cracking of methane and reported that equilibrium conversions were achieved at temperatures above 800°C. The iron oxide, also appeared to maintain some part of its activity for several hours, in contrast to a Pt/Al₂O₃ catalyst which deactivated within minutes under similar conditions. Muradov *Energy & Fuels* 12, 41 (1998) has also reported the use of carbon-based catalysts for the same reaction. Although more stable, these catalysts exhibit a lower activity. Furthermore, Ishihara et al. *Shokubai* 35,324(1993); and *Chem. Lett.*, 93(1995); reported that methane cracking takes place at low temperatures over a 10% Ni/SiO₂ catalyst, which does not deactivate even after approximately 200 carbon per nickel atoms have been deposited on it. The results reported by Ishihara, et al., however, did not demonstrate a level of efficiency of hydrogen production which would result in potential commercial use.

Summary of the Invention

It can therefore be seen from the above review of the prior art that an efficient method of directly cracking hydrocarbons to produce carbon filaments or

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fibers and hydrogen without the presence of undesirable co-products, such as carbon monoxide, has been an objective in the art.

It is therefore an object of the present invention to provide a method of producing carbon filaments or fibers and hydrogen by the direct cracking of hydrocarbons.

It is another object of the present invention to provide a method of producing carbon filaments or fibers and pure hydrogen by the direct cracking of hydrocarbons.

It is yet another object of the present invention to produce carbon filaments or fibers and high purity hydrogen by the catalytic cracking of hydrocarbons.

It is yet a further object of the present invention to provide a method of producing carbon filaments or fibers and hydrogen by direct cracking of methane through the use of a highly efficient catalyst.

It is another object of the present invention to provide a method of producing carbon filaments or fibers and hydrogen by direct cracking of methane or natural gas at low temperature using a nickel containing catalyst.

It is yet a further object of the present invention to provide a method of producing carbon filaments or fibers and high purity hydrogen by direct cracking of methane at low temperatures using a silica supported nickel-copper catalyst.

It has been discovered that the catalytic cracking of methane or natural gas as a potential route for efficient carbon filaments or fibers and hydrogen production can be accomplished over silica-supported nickel containing catalysts. In one embodiment, activity measurements for the methane cracking reaction were conducted with a 16.4 wt.% Ni/SiO₂ catalyst in a 20% CH₄ in He stream at 550°C and a gas hourly space velocity (GHSV) of 30000 h⁻¹. Under these conditions the catalyst exhibited a high initial activity for the cracking of methane (approximately 35% CH₄ conversion). Hydrogen was the only gaseous product detected. In addition, the rates of methane conversion and hydrogen formation were found to be in ratio of 1:2, thus, verifying the reaction stoichiometry for methane cracking. The amounts of carbon deposited on the spent catalyst and methane reacted indicated a good closure of the carbon balance (100±5%). The process of the invention may be

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applicable to any other suitable hydrocarbon such as ethane, ethylene, propane, propylene, butane, pentane, hexane and mixtures thereof, and hydrocarbons with molecular weights in the gasoline and diesel range. Nevertheless, it is anticipated that the preferred hydrocarbons will be methane and natural gas. During the catalytic cracking of higher molecular weight hydrocarbons, it is expected that several other undesirable products will be formed in addition to hydrogen and carbon fibers and filaments.

In a second embodiment, activity measurements for the methane cracking reaction were conducted over a set of 9 Ni-Cu/SiO₂ catalysts in which the total metal amount (on a molar basis) was maintained constant at 2.6 mmole of metal/g of support while the ratio of Ni:Cu was varied from approximately 8:1 to approximately 1:8. The reaction was carried out in a pure methane stream, at 650 and 800 °C and at a gas hourly space velocity of 6000 hr⁻¹. The results indicate that the presence of small amounts of Cu enhanced significantly the Ni activity at 800 °C. The initial conversion over the 2.3 mmole Ni/0.3 mmole Cu/SiO₂ composition for example, was measured at 63%, as compared to 14.4% for the 2.3 mmole Ni/SiO₂ composition. This is a surprising result given that Cu alone is not active for the cracking of methane under these conditions (0.3% initial methane conversion for the 0.3 mmole Cu/SiO₂ composition). The promoting effect is also more pronounced when small amounts of Cu are added (i.e., Ni:Cu ratios greater than 1). The highest initial methane conversion observed with this set of catalysts is at the 8:1 Ni:Cu ratio. Even higher initial methane conversions are expected with higher Ni:Cu ratios up to about 20:1.

Brief Description of the Drawings

For a fuller understanding of the nature and objects of the invention, reference should be made to the following detailed description of a preferred mode of practicing the invention, read in connection with the accompanying drawings, in which:

FIG. 1 represents a plot of the deactivation of a Ni/SiO₂ catalyst at 550°C and GHSV = 30,000 h⁻¹ in a stream containing 20% CH₄, in He;

FIG. 2 represents a plot of initial methane conversion as a function of catalyst composition at two different temperatures over a series of Ni-Cu/SiO₂ catalysts (○ at 650 °C and □ at 800°C).

FIG. 3 is a SEM micrograph at 25,000X illustrating the structure of the carbon fibers of the present invention.

FIG. 4 is a SEM micrograph at 50,000X illustrating the structure of the carbon fibers of the present invention.

FIG. 5 is a TEM micrograph at 100,000X illustrating the structure of the carbon fibers of the present invention.

Detailed Description of the Invention

The catalyst used in the first embodiment of this invention was prepared by incipient wetness impregnation of an aqueous solution of nickel nitrate onto the silica support, followed by calcination in air and in-situ reduction in flowing hydrogen. This is a standard method of preparation of supported metal catalysts and several different nickel salts can be used instead of nickel nitrate as the nickel precursor. Furthermore, other standard methods for the preparation of supported metal catalysts could be used without having a detrimental effect on the properties of the catalyst. In addition to silica, we investigated other inorganic supports such as alumina and titania. Although nickel supported on these supports was also found to be effective for the catalytic cracking of methane, the performance of nickel supported on silica was superior to those of the other catalysts and therefore, this system was chosen to demonstrate the invention in this application. In addition, we examined the performance of other transition metals such as Co and Fe, supported on silica for this reaction. Although these catalysts were also found to be effective for the reaction, at 550°C the performance of nickel was again superior to the other catalysts. Finally, by examining several Ni/SiO₂ catalysts of variable Ni content, it was determined that optimum performance for the catalytic cracking of methane can be obtained with a nickel content in excess of 5 wt.%, and, in particular a content of

approximately 16 wt.%. As a result, a 16 wt.% Ni/SiO₂ catalyst was chosen to demonstrate the invention in this application.

When the catalyst was placed in a conventional fixed bed reactor and exposed to a stream containing 20% CH₄ (by volume) in He, at 550°C and under a GHSV of 30,000 h⁻¹, a high initial activity was observed for the cracking of methane (approximately 35% CH₄ conversion). Hydrogen was the only gaseous product detected and the rates of methane consumption and hydrogen production were found to be in a ratio of 1:2, thus, verifying the reaction stoichiometry for methane cracking.

The catalyst used in the present invention will eventually deactivate as a result of carbon deposition. Carbon may deposit on the surface to cover the active sites (site-blocking) or accumulate at the entrance of the pores to block further access of the reactants to the interior (pore-mouth plugging). It has been estimated that in both cases catalyst deactivation would occur within a short period of time. Even if 10 carbon atoms are needed to block each surface Ni atom, for example, 11 mg of carbon deposition would be enough to completely deactivate one gram of the 16.4% Ni/SiO₂ catalyst. Furthermore, if pore-mouth plugging was the main deactivation mechanism, approximately 250 mg of carbon would be sufficient to clog the external 10% of the pores, in one gram of the Ni/SiO₂ catalyst sample.

It has been discovered that a significantly higher amount of carbon deposition on the Ni/SiO₂ catalysts occurs before deactivation occurs. At a temperature of 550°C for example, a very slow deactivation of the Ni/SiO₂ catalyst was observed for the first 2 hours (Figure 1) followed by a more rapid loss of activity during the third hour. By the time the catalyst was completely deactivated (200 minutes), approximately 0.59 g of carbon had accumulated on the 0.2 g of the Ni/SiO₂ catalyst sample. This amount is in very good agreement with the amount of carbon calculated based on the integration of the methane conversion (0.61 g), and corresponds to approximately 2700 carbon atoms accumulated on the catalyst per surface nickel atom.

It is therefore apparent that the capability of the silica supported nickel catalyst to accommodate carbon is significantly higher than those predicted by either the site-blocking or pore-mouth plugging models. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses of the spent catalysts were utilized to further understand the deactivation mechanism. SEM micrographs indicate the formation of filamentous carbon on the catalyst surface. These filaments appear to grow out of the silica support surface, with their length increasing with time-on-stream (See Figs. 3 and 4). Each filament has a bright tip, identified by the use of SEM/EDS (Energy Dispersive X-Ray Spectroscopy) to be a nickel particle. Spent catalyst samples were further studied by the use of X-Ray Diffraction (XRD). The XRD patterns, suggest that graphitic carbon constituents with different degrees of defect or distortion are present in the deactivated samples. TEM micrographs of the fully deactivated sample show that the growth of the carbon is terminated as a result of spatial limitations. The modes of filament termination include the nickel particle's restriction by the silica surface, the arm and the tip of another carbon filament. As previously described above, the formation of carbon filaments as a result of hydrocarbon cracking has been extensively reported in the literature with higher molecular weight hydrocarbons over supported nickel, iron, cobalt and several alloy catalysts. In the present invention, carbon fibers or filaments are produced preferably from the catalytic cracking of either pure methane or commercial natural gas. The type of carbon produced in the present invention is highly desirable and has added value in certain applications such as electrochemical and adsorption storage of fuel gases. The enhanced value of the carbon material from the present invention is due to its filamentous or fibrous nature, since the properties of the carbon filaments are superior to those of the ordinary carbon black. The morphology of the carbon fibers is more clearly shown in SEM and TEM micrographs, (See Figs. 3, 4 and 5).

The set of Ni-Cu/SiO₂ catalysts used in the second embodiment of this invention had the total metal amount (on a molar basis) maintained constant at 2.6 mmole of metal/g of support while the ratio of Ni:Cu was varied from approximately

8:1 to approximately 1:8. The catalysts were prepared by incipient wetness impregnation of nickel and copper nitrates ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$) obtained from Aldrich Chem. Co. Inc. (with a purity of 99.999%) onto commercially available SiO_2 (Grace Davison-Syloid 74). Prior to impregnation the silica support was dried, pressed into pellets under a pressure of 15,000 psig; crushed and sieved to obtain a granulometric fraction in the 20-35 mesh size. The impregnated samples were dried in a vacuum oven at 120 °C overnight and subsequently calcined in a muffler furnace at 700 °C for 6 hours. The Ni and Cu loadings were estimated by the weight difference between the blank support and the catalyst reduced overnight in a 1:2 H_2/N_2 mixture (total flow rate of 120 ml/min) at 650 °C.

Following the reduction treatment, the samples were exposed to methane (GHSV - 6000 hr^{-1}) at 650 and 800 °C. Activity measurements were conducted at two different temperatures and the results are presented in Fig. 4. The results indicate that the presence of small amounts of Cu enhanced significantly the initial activity at 800 °C, while the presence of Cu had no significant effect at 650 °C. The initial conversion over the 2.3 mmole Ni/0.3 mmole Cu/ SiO_2 composition for example, was measured at 63%, as compared to 14.4% for the 2.3 mmole Ni/ SiO_2 composition. This is a surprising result given that Cu alone is not active for the cracking of methane under these conditions (0.3% initial methane conversion for the 0.3 mmole Cu/ SiO_2 composition). The promoting effect is also more pronounced when small amounts of Cu are added (i.e., Ni:Cu ratios greater than 1).

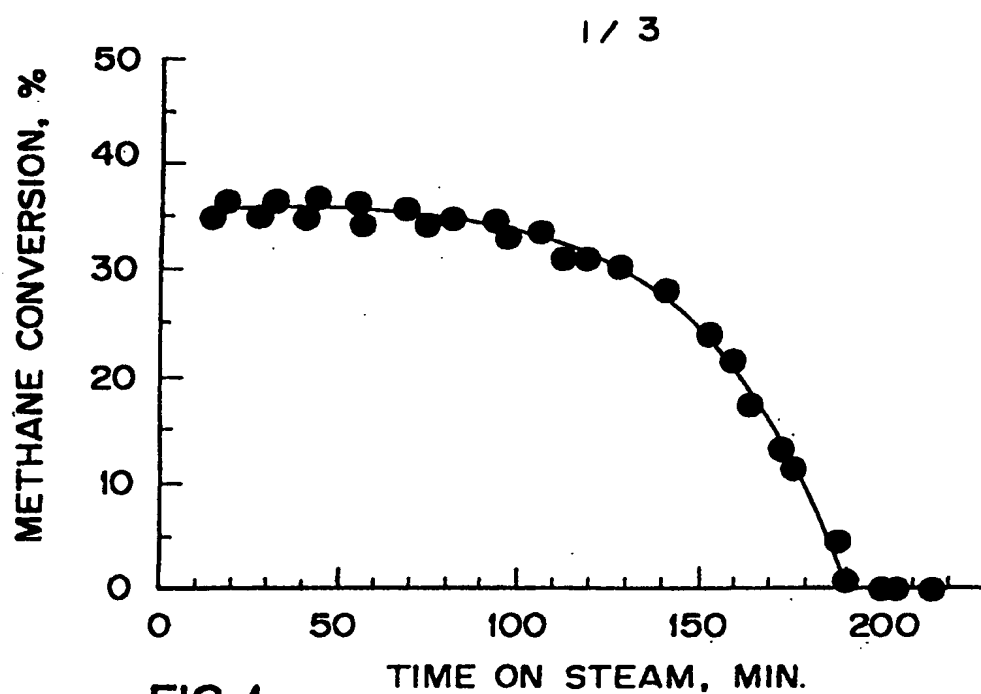
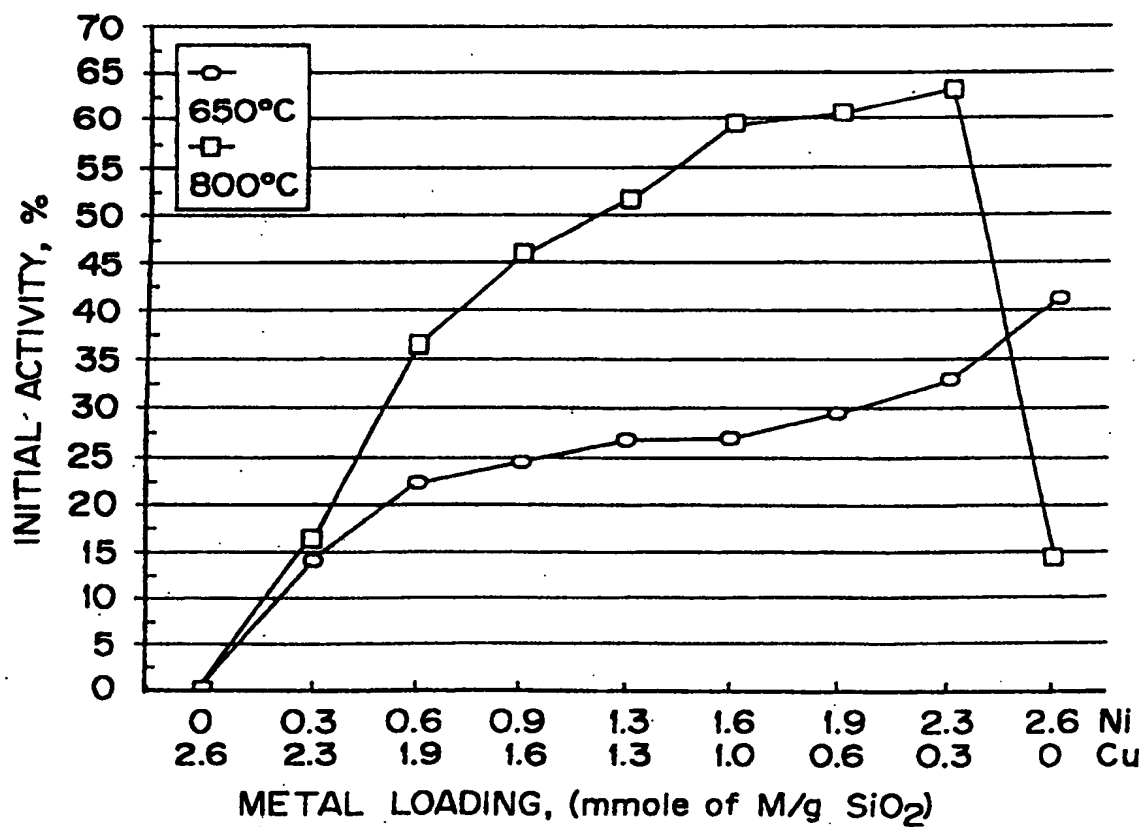
While the present invention has been particularly shown and described with reference to the preferred mode as illustrated in the drawing, it will be understood by one skilled in the art that various changes in detail may be effected therein without departing from the spirit and scope of the invention as defined by the claims.

We Claim:

- 1 1. A process for producing carbon as filaments or fibers which comprises
2 contacting a stream of a hydrocarbon with a nickel containing catalyst at a
3 temperature in the range of about 400 to 900°C which results in the conversion of
4 said gas to carbon filaments or fibers and hydrogen.
- 1 2. The process of claim 1 in which the produced carbon filaments or fibers are
2 recovered for further use.
- 1 3. The process of claim 1 in which the catalyst contains at least 5 wt.% nickel.
- 1 4. The process of claim 1 in which the catalyst further contains copper.
- 1 5. The process of claim 1 in which the nickel-copper ratio varies from about
2 20:1 to 1:8.
- 1 6. The process of claim 1 in which the catalyst is supported on an inorganic
2 support.
- 1 7. The process of claim 1 in which the catalyst is supported on silica.
- 2 8. The process of claim 1 in which the hydrogen gas is mixed with an inert
3 carrier gas.
- 1 9. A process for producing carbon filaments or fibers which comprises
2 contacting a stream of a hydrocarbon gas with a nickel containing catalyst at a
3 temperature in the range of about 400 to 900°C which results in the conversion of
4 said gas to carbon filaments or fibers and hydrogen, and where said hydrocarbon gas
5 is one selected from the group consisting of methane and natural gas.

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- 6 10. The process of claim 9 in which the produced carbon filaments or fibers are
7 recovered for further use.
- 1 11. The process of claim 9 in which the catalyst contains at least 5 wt.% nickel.
- 1 12. The process of claim 9 in which the catalyst further contains copper.
- 1 13. The process of claim 9 in which the nickel-copper ratio varies from about
2 20:1 to 1:8.
- 1 14. The process of claim 9 in which the catalyst is supported on an inorganic
2 support.
- 1 15 The process of claim 9 in which the catalyst is supported on silica.
- 2 16 The process of claim 9 in which the hydrogen gas is mixed with an inert
3 carrier gas.

**FIG. 1****FIG. 2**

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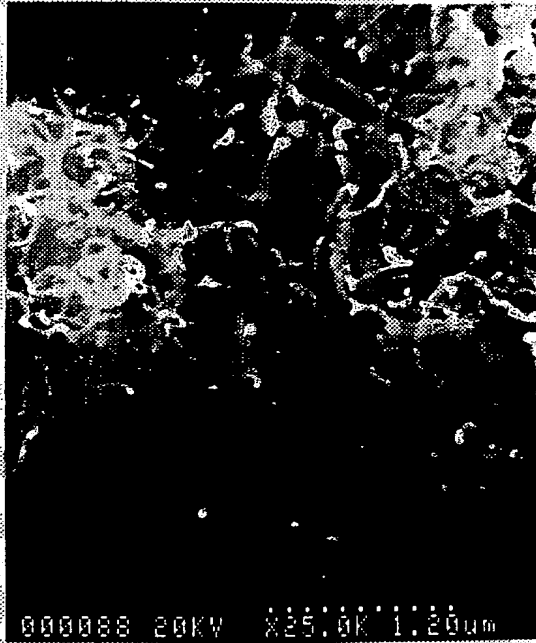


FIG. 3

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FIG. 4

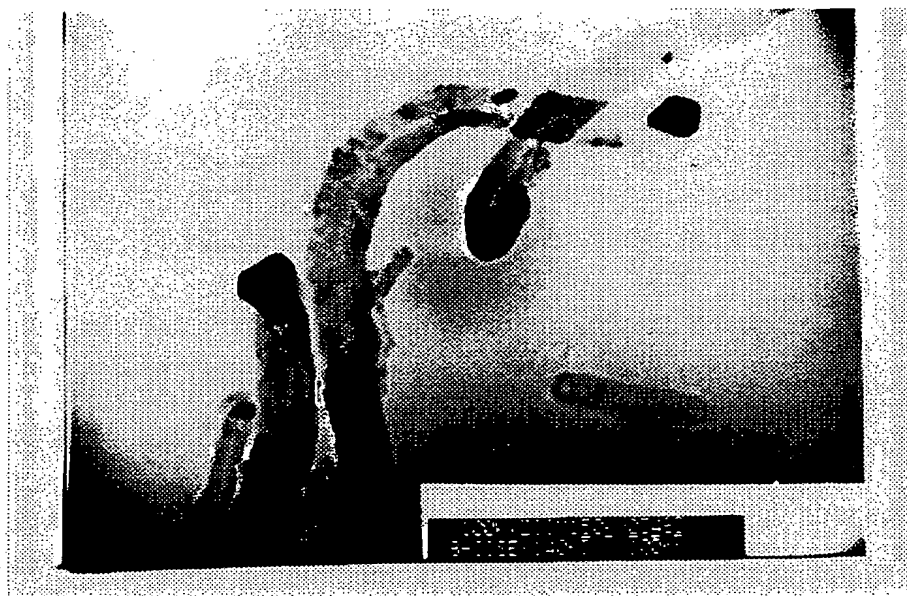


FIG. 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/03572

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B3/26 D01F9/127

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FENELONOV V B ET AL: "Structure and texture of filamentous carbons produced by methane decomposition on Ni and Ni-Cu catalysts" CARBON, vol. 35, no. 8, 1 January 1997, page 1129-1140 XP004086485 see page 1129 - page 1130 see page 1138 --- -/--	1-7,9-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 May 1999

Date of mailing of the international search report

10/06/1999

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Van der Poel, W

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/03572

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>MATSUKATA M ET AL: "Novel hydrogen/syngas production process: Catalytic activity and stability of Ni/SiO₂"</p> <p>PROCEEDINGS OF THE 1996 14TH INTERNATIONAL SYMPOSIUM ON CHEMICAL REACTION ENGINEERING. PART B;BRUGGE, BELG MAY 5-8 1996,</p> <p>vol. 51, no. 11 part B, 5 May 1996, pages 2769-2774, XP002103798</p> <p>Chem Eng Sci;Chemical Engineering Science; Chemical Reaction Engineering: From Fundamentals to Commercial Plants and Products Jun 1996 Pergamon Press Inc, Tarrytown, NY, USA</p> <p>see the whole document</p> <p>----</p>	1-3,6,7, 9-11,14, 15
X	<p>Abstracts of Papers, part 2 211th ACS National Meeting, March 24-28, 1996: T. Zhang "Deactivation and subsequent regeneration of silica-supported nickel catalysts during methane cracking"</p> <p>XP002104030</p> <p>see abstract</p> <p>----</p>	1-3,6,7, 9-11,14, 15
X	<p>US 4 435 376 A (PORTER RANDALL A ET AL)</p> <p>6 March 1984</p> <p>see the whole document</p> <p>----</p>	1-3,6, 8-11,14, 16
A	<p>DD 287 015 A (LEIPZIG CHEMIEANLAGEN)</p> <p>14 February 1991</p> <p>see the whole document</p> <p>----</p>	1-16
A	<p>DE 29 46 164 A (STAMICARBON) 3 July 1980</p> <p>see the whole document</p> <p>-----</p>	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Patent Application No
PCT/US 99/03572

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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DD 287015	A	14-02-1991	NONE	
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